

Chemistry

Lecture 7, 8

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S & P Block Elements

Outline:

- ✚ Electronic configuration
- ✚ Chemical properties of s-block elements
- ✚ Group 1 elements (Alkali metals)
- ✚ Atomic and physical properties
- ✚ Trends in reactivity
- ✚ Group 2 elements (Alkaline earth metals)
- ✚ Trends in reactivity
- ✚ Physical and chemical properties
- ✚ Group trends: atomic radii, ionic radii, Electronegativity, Ionization potential, electro-positivity or metallic character, electrical conductivity, melting and boiling points.
- ✚ Reactions of Group III elements with water, oxygen and chlorine

Introduction to Periodic Table:

- Proposed by Mosley [Based on atomic number]
- It has 7 periods represented with Arabic numerals
- Periods are horizontal rows
- 1st period has 2 elements (shortest)
- 2nd and 3rd periods have 8 elements each (short/small periods)
- 4th and 5th periods have 18 elements each (long periods)
- 6th periods has 32 elements (longest)
- 7th period has 26 elements (incomplete)
- Vertical columns are called Groups represented with Roman numerals
- They are 8 and divided into subgroups A (8) and B (10)
- There are 4 Blocks (based on valence orbital)
- s-block and p-block have normal elements, d-block $[(n-1)d^{1-10}, ns^2]$ has outer transition elements and f-block $[(n-1)d^1, (n-2)f^{1-14}, ns^2]$ has inner transition elements
- s-block $[ns^{1-2}]$ group IA and IIA elements, p-block $[ns^2, np^{1-6}]$ group IIIA-VIIIA elements (except He)
- ☞ Electronic distribution in shells gives:(only for 2,3 periods)
 - Period no. = No. of shells
 - Group no. = electrons in last shell
 - Valency = No. of binding electrons in last shell
 - Nature → less than 4 electrons in valence shell means metal otherwise non-metal

Example: ${}_7\text{N} = (2,5)$ period = 2, Group = 5, Valency = 3, Nature = Non-metal

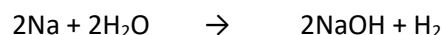
Bridge Elements: Li, Be, B, C, N, O

IA Group [Li, Na, K, Rb, Cs, Fr(radioactive)]	IIA Group [Be, Mg, Ca, Sr, Ba, Ra(radioactive)]
Exist in mineral forms	Exist in mineral forms
(valence E.C) ns^1	(valence E.C) ns^2
Oxidation state is +1	Oxidation state is +2
Monovalent	Divalent
More electropositive (high reactivity)	Less electropositive (high reactivity)
Reducing power increases down the group (except Li is strongest amongst all)	Reducing power increases down the group
Elements of IA are stronger reducing agents than IIA elements	
All IA elements form basic oxides IA elements can form normal oxides, peroxides, superoxides. Basicity increases down the group (as size of cation increases which results in increase of internuclear distance and ionization becomes easier)	IIA elements form basic oxides except Be (forms Amphoteric oxides) [Be can react with alkalies i.e. $Be + 2NaOH \rightarrow Na_2BeO_2 + H_2$] IIA elements form normal oxide and peroxide only Basicity increases down the group (as size of cation increases which results in increase of internuclear distance and ionization becomes easier)
IA elements form more basic solutions/oxides than IIA elements	
Reactivity increases down the group	Reactivity increases down the group
IA Elements are more reactive than IIA elements	
Atomic radius, Ionic radius, Metallic character, Electrical conductance, Ionic character increases down the group Only Li can form covalent bond	Atomic radius, Ionic radius, Metallic character, Electrical conductance, Ionic character increases down the group Be, Mg has can form covalent bonds
Atomic radius, Ionic radius, Metallic character, Ionic character of IA is higher than IIA elements	
Density increases down the group with exception of potassium. Cs > Rb > Na > K > Li	Density first decrease upto Calcium then increases till the end of the group Ba > Sr > Be > Mg > Ca
Density of IA elements is less than IIA elements	
Hardness decreases down the group Softer than IIA	Hardness decreases down the group Harder than IA
I.E, E.A, E.N and heat of hydration values decreases down the group due the increase in size	I.E, E.A, E.N and heat of hydration values decreases down the group due the increase in size
I.E, E.A, E.N and heat of hydration values of IA elements are less than their corresponding IIA elements	
M.P and B.P decreases down the group due to increases in size	M.P and B.P decreases down the group due to increases in size with few exceptions M.P Be > Ca > Sr > Ba > Mg B.P Be > Ba > Ca > Sr > Mg
M.P and B.P of IA elements are lower than IIA elements	
Polarizing power decreases down the group	Polarizing power decreases down the group
IIA elements have more polarizing power than IA elements	
Flame Colours	
Li (Red/Crimson red) Na (Golden yellow) K [Lilac(violet) /pink] Rb (Red /Reddish-violet) Cs (Blue)	Mg (white) Ca (Brick red/Orange-red) Sr (Crimson red/Red) Ba (Pale green/apple green)

Reactions of Group IA Elements

Reaction with Water:

- All IA elements react with water forming hydroxide along with evolution of H₂ gas



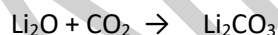
- Very rapid and exothermic reactions
- Reaction becomes increasingly vigorous from Li to Cs.
- K, Rb and Cs react with ice even at -100°C

Reaction with O₂/Air:

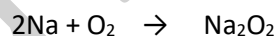
- React with O₂ or air rapidly and the surface of metal is tarnished due to formation oxide layer
- Stored in kerosene or paraffin oil
- ◆ **Li** forms lithium monoxide (normal oxide), a white solid



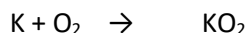
- The oxide formed reacts with CO₂ in the air to form carbonate



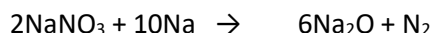
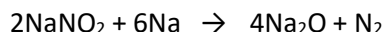
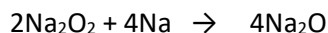
- ◆ **Na** forms normal oxide in limited supply of oxygen
- In presence of excess oxygen Na forms pale yellow peroxide



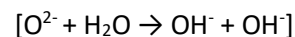
- ◆ **K, Rb, Cs** form superoxides (orange yellow)

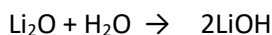


- **Cs** explodes spontaneously when in contact with air or oxygen
- ▣ Normal oxides of alkali metals other than Li are not prepared directly, so they are prepared by indirect methods i.e. by reducing peroxides, nitrates and nitrites with metal itself



- **Normal oxides** (O²⁻) [anti-fluorite structure] react with water to form hydroxide ions by proton exchange

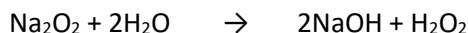




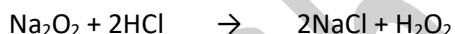
- **Normal oxides** (O^{2-}) react with HCl to form salt and water




- ✓ **Peroxides** [O_2^{2-} ($-\text{O}-\text{O}-$) $^{2-}$] strong oxidizing agent, react with water in cold conditions (as highly exothermic reaction and increase in T decomposes H_2O_2 into water and oxygen) to give hydroxide and H_2O_2



- ✓ **Peroxides** [O_2^{2-} ($-\text{O}-\text{O}-$) $^{2-}$] react with HCl (is even more exothermic than with water) to form salt and H_2O_2 which further decomposes to water and oxygen if temp. rises again



- **Superoxides** $\text{O}_2^{\cdot -}$  strong oxidizing agent [paramagnetic and coloured due to unpaired electron], react with water (highly exothermic reaction and increase in T decomposes H_2O_2 into water and oxygen) to give hydroxide and $\text{H}_2\text{O}_2 + \text{O}_2$



- **Superoxides** react with HCl (is even more exothermic than with water) to form salt and $\text{H}_2\text{O}_2 + \text{O}_2$ [H_2O_2 further decomposes to water and oxygen if temp. rises again]



Reaction with Chlorine:

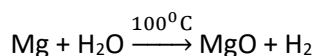
- All alkali metals react with chlorine to give chlorides [white solids] (neutral salts)
- **Li and Na** react slowly at room temp. but **molten Na** burns with brilliant yellow flame in chlorine atmosphere to form NaCl $[2\text{Na} + \text{Cl}_2 \rightarrow 2\text{NaCl}]$
- **K, Rb and Cs** react vigorously with halogens to form halides

- ✚ They all *react with hydrogen* to form hydrides (MH which are reducing agents),
- ✚ They all *react with Sulphur* to form sulphides (M_2S)
- ✚ Only Li amongst IA elements reacts with Nitrogen (to form nitride) and Carbon (to form carbide)

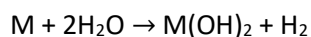
Reactions of Group IIA Elements

Reaction with Water:

- ☒ **Beryllium** does not react even at red hot temperature
- ☒ **Magnesium** reacts slowly with boiling water and quite rapidly with steam

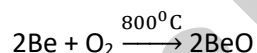


- Very clean Mg ribbon has very slight reaction with cold water. After several minutes bubbles of H_2 gas evolve. However the reaction soon stops because magnesium hydroxide formed almost insoluble in water and forms a barrier for Mg preventing further reaction
- ☞ **Calcium, strontium and barium** produce hydroxide with water (exothermic reactions)

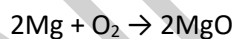


Reaction with Air/Oxygen:

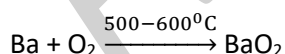
- ☞ IIA elements when burnt in oxygen form **normal oxides except Barium** (forms peroxide)
- ☞ **Sr can also form peroxide** if burnt in oxygen **under high pressure**
- ☞ **Beryllium (Be)** is resistant to complete oxidation due to stable layer of BeO
- ☞ It oxidizes rapidly at about $800^\circ C$



- ☞ Not tarnished by atmosphere but soon **loses silvery appearance**
- ☞ **Magnesium (Mg)** quickly becomes coated with MgO layer which protects it from further corrosion at ordinary temperature

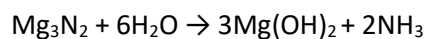
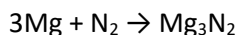


- ☞ Mg burnt in air produces small amount of nitride (Mg_3N_2) along with MgO
- ☞ **Barium (Ba)** forms peroxide

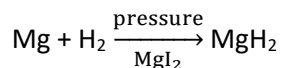


Reaction with Nitrogen:

- ☞ IIA elements react with nitrogen to give nitrides
- ☞ Nitrides hydrolyze vigorously with water giving ammonia and respective hydroxide



- IIA elements in molten form react with hydrogen under high pressure to give hydrides



- IIA elements react with sulphur to give metal sulphides (MS) which on hydrolysis liberate H_2S
- IIA elements react with halogens to give metal halides (MX_2)

Thermal Decomposition and Solubility of compounds of IA

Oxides:

- All are soluble in water giving respective hydroxides
- It is an **acid base reaction** which involves decomposition of water by oxide ion
- **KO₂** absorbs CO₂ while giving off O₂ gas at same time, therefore used in breathing equipment

Hydroxides:

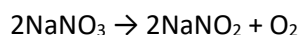
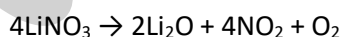
- All are crystalline solids
- Generally hygroscopic
- All are soluble in water except LiOH
- All are stable to heat except LiOH which decomposes to Li₂O + H₂O

Carbonates:

- All are soluble in water except Li₂CO₃
- All are stable to heat except Li₂CO₃ [gain of electrostatic attraction in converting from carbonate to oxide is considerable in case of Li⁺ ion not for other large sized ions]
- They decompose to give respective oxides $\text{Li}_2\text{CO}_3 \rightarrow \text{Li}_2\text{O} + \text{CO}_2$
- **Sodium carbonate:** Below 35.2°C it crystallizes out as Na₂CO₃·10H₂O called washing soda [on standing in air it slowly loses water and convert to white powder Na₂CO₃·H₂O] and above 35.2°C it crystallizes out as Na₂CO₃·H₂O

Sulphates/Nitrates:

- All sulphates and nitrates are soluble in water
- Lithium nitrate decomposes differently from rest



Thermal Decomposition and Solubility of compounds of IIA

Oxides:

- Lattice energy decreases down the group
- Solubility increases down the group
- **BeO and MgO are insoluble** while others are soluble and react with water to give hydroxides
- **BeO** is Amphoteric oxide while rest are basic
- Due to small size of Be⁺² ion, BeO is covalent while others are ionic
- It is harder than others with high M.P than other oxides
- Each Be is tetrahedrally coordinates with 4 O-atoms

Amphoteric oxides [Be (IIA), Zn (IIB), [Al, Ga, In] (IIIA), [Ge, Sn, Pb] (IVA), [As, Sb, Bi] (VA)]

Hydroxides:

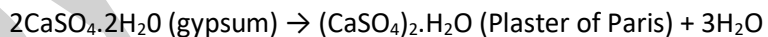
- Lattice energy decreases down the group
- Solubility increases down the group
- **Be(OH)₂ insoluble, Mg(OH)₂ sparingly soluble** while others are soluble
- They decompose to give respective oxides $\text{Mg(OH)}_2 \rightarrow \text{MgO} + \text{H}_2\text{O}$
- Ease of decomposition increases down the group
- Be(OH)₂ is Amphoteric while others are basic hydroxides
- It is covalent (due to small size of Be⁺² ion) while others are ionic
- Saturated solution of Ca(OH)₂ in water is **Lime water** used as test for CO₂
- Suspension of Mg(OH)₂ in water is **Milk of magnesia** used for treatment of acidity of stomach
- Suspension of Ca(OH)₂ in water is **Milk of lime** used as white wash

Carbonates:

- Lattice energy increases down the group
- Slightly soluble in water
- Solubility decreases down the group
- They decompose to give respective oxides $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
- Ease of decomposition decreases down the group

Sulphates:

- Lattice energy increases down the group
- Solubility decreases down the group
- **BeSO₄, MgSO₄ are fairly soluble, CaSO₄ is slightly soluble**
- **SrSO₄ and BaSO₄ are almost insoluble**
- Ease of decomposition decreases down the group
- Gypsum on heating above 100°C loses 3 quarters of water of crystallization to give Plaster of Paris



Nitrates:

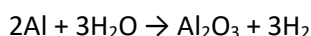
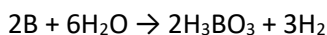
- Soluble in water
- On decomposition produce O₂, NO₂ and metal oxide



Reactions of Group IIIA Elements

Reaction with Water:

- Neither B nor Al react with water at room temp. but both react with steam to liberate H₂ gas
- Aluminium reacts in powder form



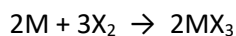
- Inertness of Al is due to protective oxide layer [reaction is very slow due to layer that build up even during reaction]
- In the absence of oxygen, gallium and indium are unaffected by water.
- Thallium the most metallic elements of IIIA reacts slowly with hot water and readily with steam to produce thallium oxide (Tl₂O)
- Thallium forms poisonous thallium hydroxide [TlOH] in moist air in presence of oxygen

Reaction with Oxygen:

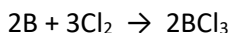
- Only thallium is affected by air at room temp. and thallium (III) oxide is slowly formed
- All the elements however burn in air when strongly heated and with exception of gallium form the oxide M₂O₃; gallium forms a mixed oxide of composition GaO
 - $4\text{B} + 3\text{O}_2 \rightarrow 2\text{B}_2\text{O}_3$ $2\text{B} + \text{N}_2 \rightarrow 2\text{BN}$
 - $4\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3$ $2\text{Al} + \text{N}_2 \rightarrow 2\text{AlN}$
- Reactivity increases down the group; boron is unreactive in crystalline form but reacts in finely divided form
- Aluminium powder is heated at 800°C and above, the metal will react with air to form Al₂O₃, AlN. The reaction is accompanied by evolution of heat and intense white light (used in flash light photography and thermite process)
- Because of ability to combine with oxygen, nitrogen aluminium is used to remove air bubbles from molten metals

Reaction with Chlorine:

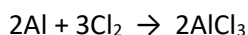
- React with halogens at high temperature to form tri-halides (MX₃)



- Boron forms covalent liquid boron trichloride on heating in chlorine gas



- Aluminium burns with stream of chlorine when passed over heated aluminum foil to produce very pale yellow aluminum chloride (polymeric halide) [BeCl₂, AlCl₃, GaCl₃ are polymeric halides]



Atomic Radius

- ☞ Average distance between nucleus and valence electrons, can be measured as covalent radius
- ☞ Covalent radius = half of bond length of homo-atomic molecule

Periodic Trend:

Down the Group:

- Down the group no. of shells, shielding effect increases and effective nuclear charge decreases
- Hold of nucleus on valence electrons decreases and size increases

Along the Period:

- Along the period no. of shells, shielding effect remains same and nuclear charge increases
- Hold of nucleus on valence electrons increases and size decreases

📊 Maximum radius is of IA and minimum is of VIIIA [same period]

Ionic Radius

- ☞ Size of an ion while considering it to be spherical in shape

Periodic Trend: Same as of Atomic Radius

◆ Cation:

- Formed by loss of electrons
- Size of cation < size of parent atom i.e. Na = 186 pm, $\text{Na}^{+1} = 102$ pm (Check it from latest addition of text book)
- Larger the positive charge, smaller is the radius (no. of shells should be same)
- $\text{Li}^{+1} > \text{Be}^{+2} > \text{B}^{+3}$ (iso-electronic)

◆ Anion:

- Formed by gain of electrons
- Size of anion > size of parent atom i.e. F = 72 pm, $\text{F}^{-1} = 133$ pm (Check it from latest addition of text book)
- Larger the negative charge, larger is the radius (no. of shells should be same)
- $\text{N}^{-3} > \text{O}^{-2} > \text{F}^{-1}$ (iso-electronic)

$$r_{-} > r_{\text{vander waal}} > r_{\text{covalent}} > r_{+}$$

Melting and Boiling Points

Along the Period:

- Increases from IA to IVA and then decreases from VA to VIIIA
- It is because;

- ☞ No. of bonding electrons increases up to IVA and then decreases from VA to VIIIA (Bonding changes)
- ☞ IA-IVA elements usually exist as giant/large molecules
- ☞ While VA-VIIIA elements are simple molecules with weak intermolecular forces

Down the Group:

- Usually decreases down the group but in case of VIIA and VIIIA, it increases down the group
- It is because;
 - ☞ Down the group polarizability increases due to size increase
 - ☞ As a result London forces increase

Exceptional Cases:

- Group IIA has; **Be > Ca > Sr > Ba > Mg** (due to loose hexagonal packing in Mg)
- **S > P** because sulphur exists as **S₈** and phosphorous as **P₄**

Ionization Energy (I.E)

Def: Minimum amount of energy required to remove valence electron of an isolated gaseous atom

- Measured in KJmol^{-1}
- Property of an element in free state

Factors:

- Atomic size inversely related to I.E
- Shielding effect inversely related to I.E
- Nuclear charge directly related to I.E
- Nature of orbital
 - ☞ **s > p > d > f** (I.E/Penetration order)
 - ☞ Because s orbital is of small size with more penetrating power than all others
- Stable electronic configuration directly related to I.E
- **3rd I.E > 2nd I.E > 1st I.E**

Periodic Trend:

- Decreases down the group due to increase in size (size explained in atomic radius)
- Increases along the period due to decrease in size (size explained in atomic radius)

Exceptional Cases:

- Only along period i.e.
 - **IIA > IIIA and VA > VIA**
 - It is due to stable electronic configuration
- 📊 Stability order for orbitals: **Completely filled > half filled > partially filled**

- ☞ $IA < IIIA < IIA < IVA < VIA < VA < VIIA < VIIIA$ (Along the period)
- ☞ $ns^1 < np^1 < ns^2 < np^2 < np^4 < np^3 < np^5 < np^6$
- ☞ Ionization energy will increase with increases in positive charge (when iso-electronic)
- ☞ Al^{+2} , Mg^{+1} , Na^{+1} , Ne^{+1} which has maximum I.E?

Applications:

- Metallic character
 - Low I.E means metal, High I.E means non-metal
 - Valency (difference b/w I.E's values)

Electron Affinity (E.A) [Just read not directly in outline]

Def: Energy change when an electron is added to valence shell of an isolated gaseous atom

- Measured in $KJmol^{-1}$
- Property of an element in free state
- Usually 1st E.A is negative with few exceptions $O + 1e^- \rightarrow O^-$ E.A = $-141 kJmol^{-1}$
- 2nd E.A is positive as energy is req. to add 2nd electron to overcome the repulsion for incoming electron $O^- + 1e^- \rightarrow O^{2-}$ E.A = $+744 kJmol^{-1}$

Factors:

- Atomic size inversely related to E.A
- Shielding effect inversely related to E.A
- Nuclear charge directly related to E.A
- Nature of orbital
- Stable the electronic configuration inversely related to E.A
 - ☞ IIA, IA \rightarrow positive values of E.A
 - ☞ Nitrogen (VA) \rightarrow very small values nearing zero
 - ☞ Noble gases \rightarrow Nearly zero/positive values
 - ☞ Halogens \rightarrow Highest values in table

Periodic Trend:

- Decreases down the group due to increase in size (size explained in atomic radius)
- Increases along the period up to VIIA due to decrease in size (size explained in atomic radius)

Exceptional Cases:

- Period IIIA elements have more E.A values than their respective period IIA elements like $Cl > F$, $S > O$, $P > N$ etc.
- Halogens $\rightarrow Cl > Br > F > I$
- IIA elements have low E.A than IA elements and VA elements less than IVA elements

Electronegativity (E.N)

Def: Ability of an atom to attract shared pair of electrons towards itself

- No unit
- Property of an element in combined state
- It is a relative term
- Related to I.E and E.A
- Same atoms i.e. H-H \rightarrow zero E.N difference
- Different atoms i.e. H-F \rightarrow E.N difference exists

Factors and effect same as for I.E and E.A

Periodic Trend same as for I.E and E.A

Applications:

- 📊 E.N difference gives;
- Bond energy
 - Dipole moment
 - Ionic/Covalent character
 - ☞ If E.N difference equal or less than 0.4 (Non-polar covalent)
 - ☞ If E.N difference > 0.4 but < 1.7 (Polar covalent)
 - ☞ If E.N difference > 1.7 (Ionic)
 - ☞ If E.N difference = 1.7 (50 % each ionic and covalent)

Electrical Conductance

Def: Tendency to conduct electricity due to free electrons in the structure

- It depends upon;
 - Presence of loose electrons in valence shell
 - Easy removal of loose electrons to form electronic cloud within structure

Periodic Trend:

- IA, IIA, IIIA (except B) show excellent conductivity which increases down the group
- However, this trend is not free from individual variations
- Metals of group IB (coinage metals i.e. Ag $>$ Cu $>$ Au) are extraordinary values of electrical conductance
- Non-metals of VIA and VIIA show low values electrical conductance that they are considered bad conductors or insulators
- Transition elements show very abrupt change in electrical conductivity
- Carbon in form of Diamond is insulator (All 4 valence electrons are tetrahedral bonded)

- Carbon in form of Graphite is conductor (one of 4 electrons is not bounded i.e. free electrons in layers)
- Lower members of IVA (Sn, Pb), VA (Bi) are metals with good electrical conductivity values comparable with IA

Special Case:

In period 3, the electrical conductance increases from **Na to Mg till Al has maximum** and then suddenly decreases onwards

Electro positivity or Metallic character

- Tendency of element to lose electron is called metallic character
- Elements of periodic table are divided into metals, non metals and metalloids
- **Metals:** Good conductors of heat and electricity
Tendency to lose electron to form cation
Form basic oxides which gives bases when dissolved in water
- ✓ **Down the Group:** Increases as removal of electron becomes easier due to increase in size
- ✓ **Across the Period:** Decreases as removal of electron becomes difficult due to decrease in size
- **Non-Metals:** Poor conductors of heat and electricity
Tendency to gain electron to form anion
Form acidic oxides which gives acids when dissolved in water
All gases are non metals
- ✓ **Down the Group:** Decreases due to increase in size [F > Cl > Br > I]
- ✓ **Across the Period:** Increases due to decrease in size



CO, NO, N₂O, H₂O are neutral oxides